

PCT

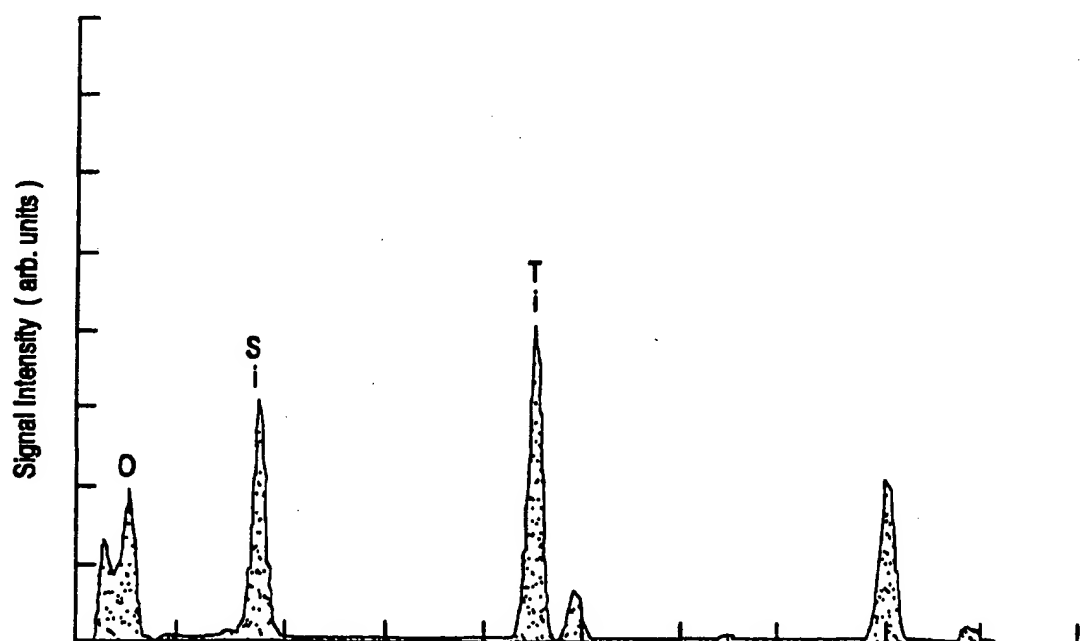
WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <p>(51) International Patent Classification ⁶ : C23C 16/40, B29D 11/00</p> | <p>A1</p> | <p>(11) International Publication Number: WO 98/39496 (43) International Publication Date: 11 September 1998 (11.09.98)</p> |
| <p>(21) International Application Number: PCT/US98/03656 (22) International Filing Date: 25 February 1998 (25.02.98) (30) Priority Data: 60/040,048 7 March 1997 (07.03.97) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BLACKWELL, Jeffery, L. [US/US]; 289 W. William Street, Corning, NY 14830 (US). DASHER, David [US/US]; 137 Field Street #45, Corning, NY 14830 (US). SUTTON, A., Renee [US/US]; 25 1/2 Earl Street, Corning, NY 14830 (US). TRUESDALE, Carlton, M. [US/US]; 11922 River Road, Corning, NY 14830 (US). (74) Agent: HERZFELD, Alexander, R.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).</p> | | <p>(81) Designated States: JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i></p> |

(54) Title: METHOD OF MAKING TITANIA-DOPED FUSED SILICA



Transmission Spectrum of TYZOR DC

(57) Abstract

This invention relates to production of high purity fused silica glass doped with titania using titanium chelates. Useful chelates include titanium acetylacetonate, and titanium ethyl acetoacetate among others.

METHOD OF MAKING TITANIA-DOPED FUSED SILICA

FIELD OF THE INVENTION

5 The invention relates generally to the manufacture of high purity metal oxide glass, and specifically to a method of doping high purity fused silica using organotitanium materials.

BACKGROUND OF THE INVENTION

10 Titania-doped silica glasses have found numerous use in the industry due to its low expansion properties as well as for its excellent resistance to fatigue. In addition, optical fiber having one or more outer layers doped with titania has been shown to exhibit superior strength, as compared to homogeneous silica clad fibers. Superior strength is desirable in optical fiber as it reduces the potential for rupture and
15 consequential replacement.

 Various methods and apparatus for the production of high purity metal oxides, and particularly fused silica, from a chloride-based feedstock have been well documented. Such equipment generally include a number of burner arrangements and feedstock delivery systems, all based on the oxidation of a metal chloride through flame
20 hydrolysis or pyrolysis. Illustrative examples are, U.S. Pat. No. 4,491,604 (Lesk et al.) wherein trichlorosilane, dichlorosilane, and silicon tetrachloride are flame hydrolyzed to form soot, and U.S. Pat. No. 3,666,414 (Bayer) wherein silicon halides, such as silicon chloroform, are flame hydrolyzed. In similar processes, U.S. Pat. Nos.

tetraethoxysilane, though none of the halide-free titania-containing source compounds of the instant invention are mentioned.

Recently, various methods have been suggested for the manufacture of titania-doped silica. For example, co-assigned, U.S. Patent No. 5,067,975, disclosed a method of doping silica with titania using SiCl_4 and TiCl_4 for optical fiber applications. The resulting optical fiber includes a core, an inner cladding, and two outer claddings, one nominally about 8% by weight TiO_2 and a bump layer, with the bump layer having a TiO_2 concentration greater than 10.5 % by weight. The sole purpose of the bump layer being to control the loss of titania during consolidation.

More recently, co-assigned U.S. Patent No. 5,154,744, disclosed a method of doping silica with titania which method eliminates the need for the bump layer without compromising the strength of the fiber. This patent discloses a method of making titania-doped silica glass having excellent fatigue resistance as well as excellent retention of titania after consolidation, by extracting titania from organometallic compounds selected from titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra 2-ethylhexyloxide, titanium tetra cyclopentyloxide, and titanium amides.

While the methods disclosed in the above patents have been found adequate for the production of titania-doped fused silica, there continues to be a need for more efficient methods of producing such products. In particular, there is an ongoing need for methods which can be used to produce titania-doped fused silica of improved physical properties.

SUMMARY OF THE INVENTION

Briefly, the invention relates to a method of making titania-doped fused silica using a group of organotitanium materials which are less sensitive to air and moisture, and which tend to decompose less than previously disclosed organotitanium materials.

In one aspect, the invention relates to a method of making a non-porous body of high purity fused silica glass doped with titania comprising the steps of:

- (a) forming amorphous particles of high purity fused silica;
- (b) doping said particles with titania in vapor form;
- (c) depositing said titania-doped amorphous particles onto a support; and

A two-step process has also been described for the production of doped fused silica. In the first stage, oxygen or nitrogen, the carrier gas, is bubbled through a liquid feedstock of titania and silica precursors. For example, the feedstock may contain titania precursors such as titanium tetra isopropoxide, titanium tetra ethoxide, titanium tetra 2-ethylhexyloxide, titanium tetra cyclopentyloxide, titanium amides and silica precursor such as octamethylcyclotetrasiloxane (OMCTS), maintained at a constant temperature. In one useful embodiment, two feedstock of titania and silica precursors are heated to temperatures in the range of 100-170 °C to generate vaporous reactants. The resulting vaporous reactant are transported to a reaction site, such as a burner, via the carrier gas, wherein the vaporous gas streams are combusted in a burner flame fueled with natural gas and oxygen. The presence of oxygen serves to convert the vaporous reactants to their respective oxides upon exiting the burner orifice to form a stream of volatile gases and finely-divided, spherical particles of soot that are deposited onto a substrate, forming a porous blank, or preform, of opaque, white silica soot. In the second stage, the blank, or preform, is heat treated in a helium/chlorine atmosphere to full consolidation. For optical fiber production, there is a third and final stage in which conventional fiber-draw technology is utilized to pull optical waveguide fiber from the consolidated preform.

In one particularly useful process to which the present invention can be adapted, two raw materials, titania and silica precursors, are separately delivered to a furnace via two tanks. The tanks are maintained at appropriate temperatures to vaporize the raw materials. The vapors are then carried to an udder where they are mixed and burned with oxygen to produce silicon and titania dioxides. In one example, the vapors are carried from the tanks to the udder by flowing a nitrogen gas through the tanks at flow rates appropriate for a given operation. The size of the tanks, as well as the temperature of the raw materials tanks can also vary depending on the vaporization particular raw materials and the desired level of production.

The present method can also be adapted to other fused silica manufacturing processes such as described in U.S. Pat. Nos. 5,043,002, herein incorporated by reference. The inventive process can also be adapted to known methods of producing high purity fused silica by flame pyrolysis or hydrolysis, such as those disclosed in the

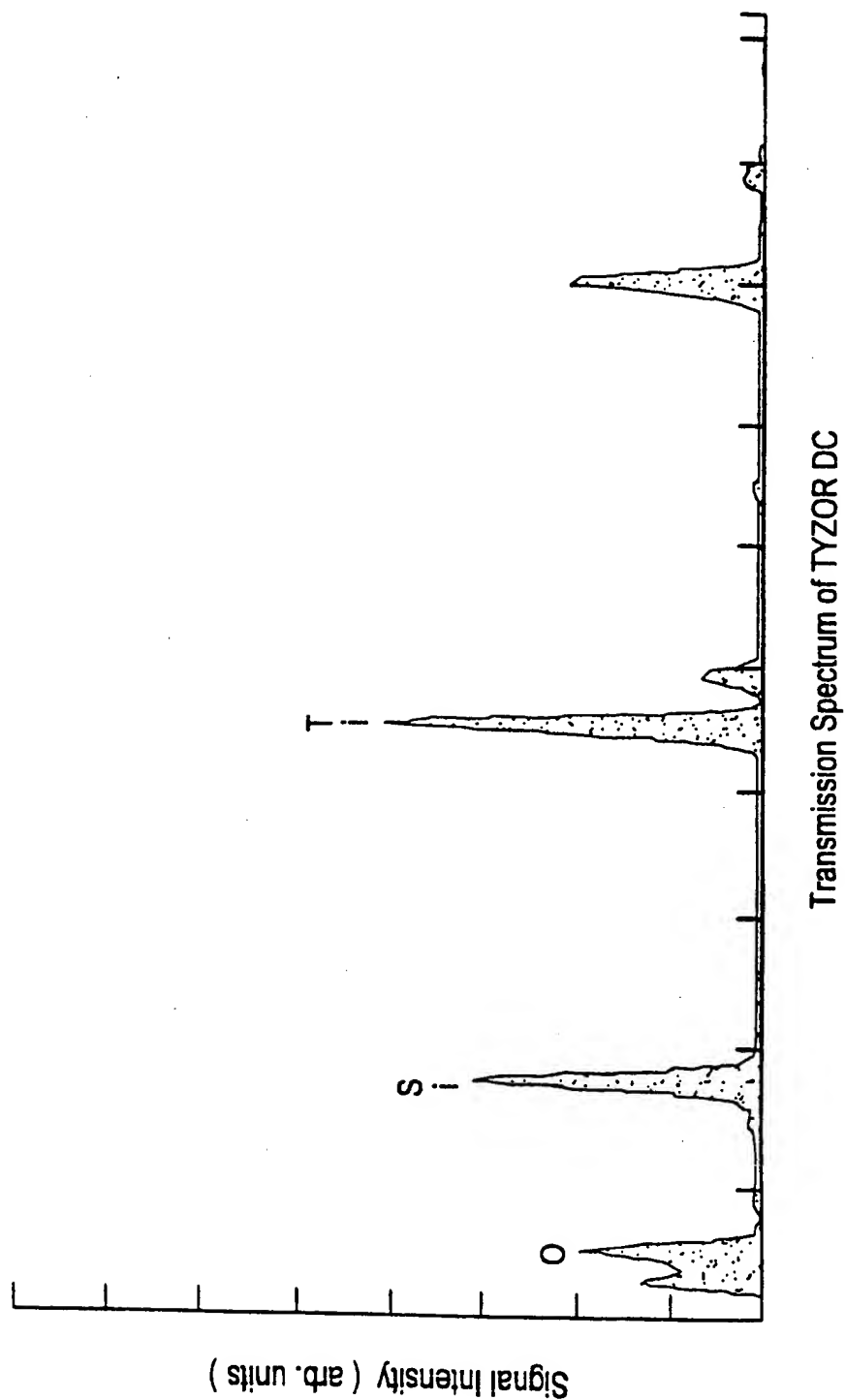
have found that the above problems are significantly reduced if not eliminated by the use of the organotitanium materials described below.

We have discovered a group of organotitanium materials, titanium chelates, which are compatible with OMCTS, less sensitive to air and moisture, and which tend to decompose less than titanium isopropoxide. By compatible, we mean that the titanium chelate does not polymerize itself or with the silica precursor as polymerization leads to a decrease in the vapor pressure, and in the absence of vaporization the result is a decrease in the amount of titania soot collected. Any titanium chelate which is compatible with the silicon precursor, is relatively insensitive to both air and moisture, and which will not prematurely decompose or polymerize, may be used in the present method. Conventional organotitanium materials such as titanium isopropoxide have a tendency to prematurely breakdown (decompose) before the end of the processing period (less than 7 days and in some cases, less than 4 days). The ideal processing time is about 6 to 7 days, preferably, 160 hours. We have found that the inventive chelate materials are able to withstand the operating temperatures for prolonged periods of time and as such do not show the premature decompositions observed in conventional alkoxide materials. Preferred titanium chelates are those having a boiling point of 250 °C or less. We have found one class of titanium chelates, the amines, and in particular titanium diethanolamine to be incompatible with siloxanes, in particular, OMCTS. Other titanium chelates which are not useful for the present invention include titanium di(dioctylpyrophosphate) oxyacetate, titanium di(butyl, octylpyrophosphate) di(dioctyl, hydrogen phosphite) oxyacetate. These compounds exhibit low volatility and are unacceptable because they are likely to introduce phosphorous into the glass. Another compound which is not particularly preferred is titanium tetra acetate, a low volatility solid.

Examples of useful titanium chelates include, titanium acetylacetonates, and titanium ethyl acetoacetates in particular bis(ethylacetoacetato) diisopropoxy titanate (TYZOR® DC) and acetylacetonate titanate chelate (TYZOR® GBA) both available from DuPont, Wilmington, Delaware. In addition to being compatible with OMCTS, these chelates are also generally miscible with the silica precursors.

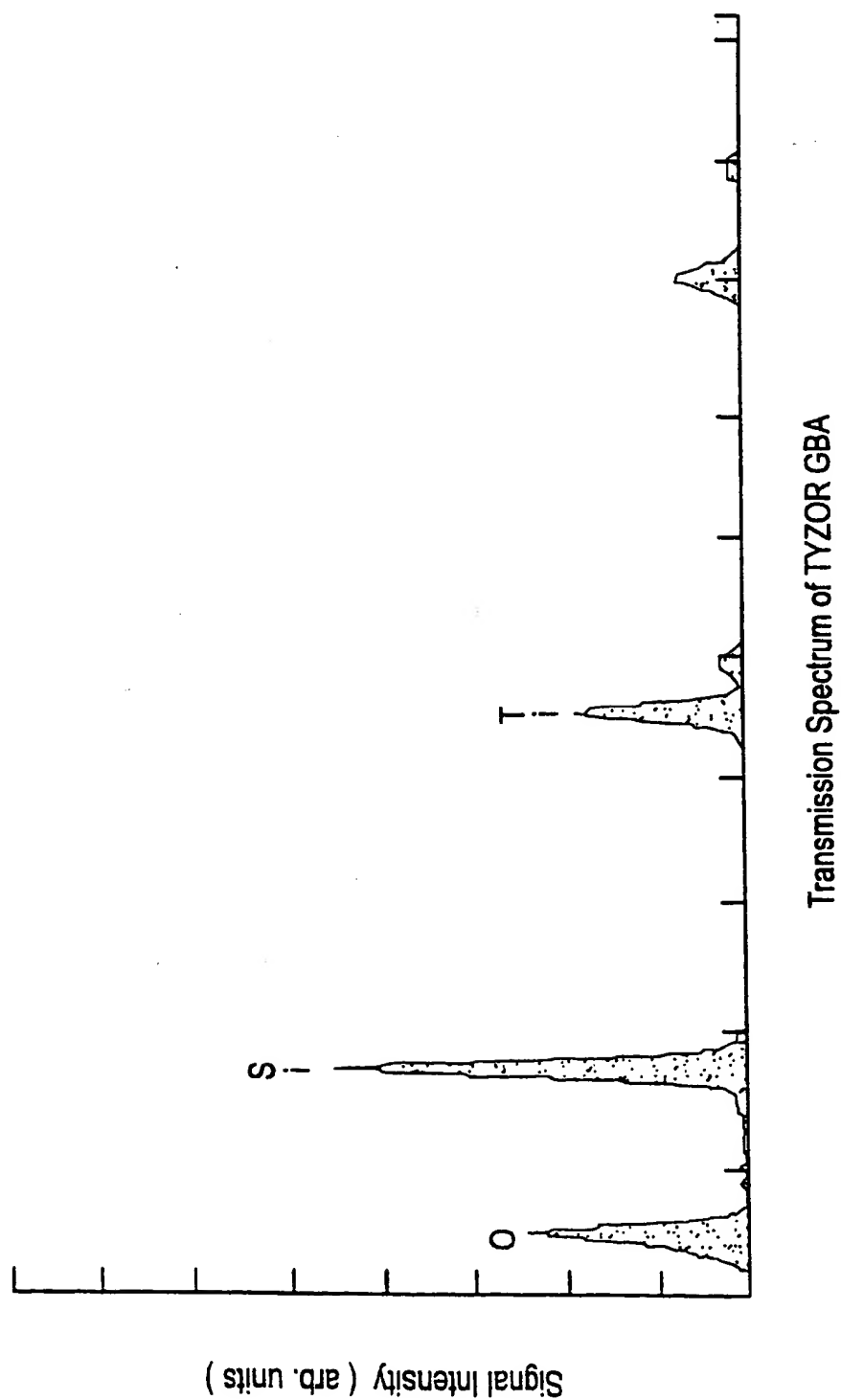
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FIG. 1



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FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03656**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C23C 16/40; B29D 11/00

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/163, 163.2, 166, 167, 452, 453, 255.2, 255.3, 255; 423/326, 336, 337, 610, 598; 264/1.24, 1.28, 81; 65/413

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US 5,154,744 A (BLACKWELL et al.) 13 October 1992 (13-10-92), column 1, lines 53-68; column 2, lines 60-68; column 4, lines 34-55; column 5, lines 2-7 and 25-43. | 1-7 |
| Y | Lee et al., Preparation and Characterization of Titanium(IV) Oxide Photocatalysts, Materials Research Bulletin, June 1992, Vol. 27, No. 6, pp. 685-692, especially p. 686. | 1-7 |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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|---|--|
| * Special categories of cited documents | *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| *A* document defining the general state of the art which is not considered to be of particular relevance | *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| *E* earlier document published on or after the international filing date | *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | *Z* document member of the same patent family |
| *O* document referring to an oral disclosure, use, exhibition or other means | |
| *P* document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search

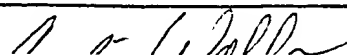
14 MAY 1998

Date of mailing of the international search report

09 JUN 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks

Authorized officer



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/03656

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 8
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.